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IN THE PROCESS OF METAMORPHISM

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FACILITY FORM 602

N 66-11604

(ACCESSION NUMBER)

24

(PAGES)

(THRU)

(CODE)

(CATEGORY)

(NASA CR OR TMX OR AD NUMBER)

GPO PRICE \$

CFSTI PRICE(S) \$

Hard copy (HC) 1.00

Microfiche (MF) 50

ff 653 July 65

Translated from Geologichniy Zhurnal,
Akademiya Nauk Ukrainskoy RSR, Vol. 24, No. 5,
pp. 16-29, 1964.NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON
NOVEMBER 1965

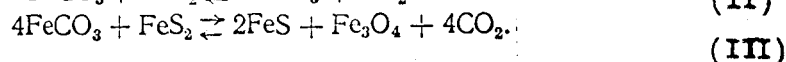
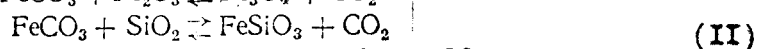
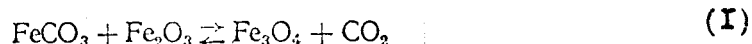
THEORETICAL DATA ON THE STABILITY OF SIDERITE
IN THE PROCESS OF METAMORPHISM

by Yu. P. Mel'nik

The carbonates of the isomorphous series $\text{FeCO}_3\text{-MgCO}_3$ which are widespread in the pre-Cambrian ferrosilicon formations, particularly siderite and sideroplesite, played an important part in the metamorphic process of mineral formation. The importance of siderite as a probable outcrop of the primary sedimentary or diagenetic iron mineral, transformed into the chief ore mineral of ferruginous quartzites and jaspilites, magnetite, was frequently emphasized in geological literature [1, 7, 11, 20, 21 and 26]. But the hypothesis of the primary sedimentary genesis of magnetite [17, 27, 28, 35 and 37] and the formation of magnetite in the metamorphism of hydrous ferric oxide or hematite [31 and 32] has recently gained wide credence.

The problem of the genesis of magnetite in the metamorphosed ferruginous rocks is closely associated with the stability of its possible outcropping products -- siderite, hydrous ferric oxide and hematite. We shall confine ourselves further on to a detailed theoretical study of siderite stability as temperature, pressure and concentration functions (expressed in terms of volatility) of the possible basic components-- H_2O , CO_2 , O_2 , CO and H_2 --in the metamorphic fluids, and a brief discussion of hematite stability in the conditions of its transformation into magnetite.

The information on siderite stability in conditions of metamorphism, found in geological literature, is based primarily on mineralo-petrographic observations and, to a lesser extent, on thermographic investigations. Theoretical and experimental data on siderite stability at high temperature and under great pressure are quite limited. Only D.S. Korzhinskiy's study [13] contains the curves $P_{\text{CO}_2} \text{ of } (T)$ which were first calculated by Goldschmidt for certain reactions with siderite:



These curves were later included in a number of monographs and even textbooks [2, 9], despite the fact that Goldschmidt's calculations were based on inaccurate thermodynamic

magnitudes, and now require considerable corrections on the basis of the new data. It is also quite clear that the cited reactions do not in any way exhaust all the possible methods of transforming siderite, and cannot be used as a basis for plotting a stability diagram in coordinates $T - P_{\text{CO}_2}$. Furthermore, the commonly accepted methods of constructing a carbonate stability diagram as a mere function of partial CO_2 pressure does not enable us to prove the important role of H_2O and CO_2 as possible oxidizers, and include H_2O as well as CO and H_2 in the number of variables determining the boundaries of iron-ore mineral stability.

We have made thermodynamic calculations of the equilibrium constants of all possible thermal dissociation reactions and the theoretically valid reduction - oxidation reactions involving the use of siderite and its decay products. The resulting data were used for the construction of diagrams of the siderite stability fields and its alteration products-- FeO , Fe_3O_4 and Fe_2O_3 -- as the temperature and concentration (volatility) functions of the components in the metamorphic fluids. The curves $P_{\text{CO}_2} = f(T)$ of the above-cited Goldschmidt-Korzhinskiy reactions were also defined more precisely. The results obtained show the importance of water and carbonic acid as high-temperature oxidizers in the metamorphic processes.

The thermodynamic calculation methods

The methods of thermodynamic calculations of chemical processes, including the processes that are taking place in the earth's crust [4,6,15, 18 and 19], are dealt with in voluminous literature. In some of the publications, the methods of calculating the constants of the reaction equilibrium (K) are presented as temperature functions.

The finite equations recommended for these calculations by various authors may be different in form, but in most cases they are based on the initial equation of the isotherm reaction:

$$\ln K = - \frac{\Delta Z^*}{RT}$$

* The symbols for the thermodynamic magnitudes everywhere are those proposed by V. A. Kireyev [1].

The magnitude of the changing free energy or Gibbs potential (ΔZ) of the investigated reaction at an unknown temperature (T) can be determined with various degrees of accuracy, depending on whether the changing thermal capacity of the reaction and the changing thermal capacities of the component-temperature reaction are taken into account.

In the calculations used in this study, the equilibrium constants of the metamorphic reactions at unknown temperatures are determined by the equations of the reaction isobars:

$$\ln K = \int \frac{\Delta H}{RT^2} dT,$$

which was integrated after the substitution of equation $\Delta H = f(T)$ which was different from the accepted degree of accuracy. The conclusions and final form of the obtained formulas are presented in greater detail in our previous study [16].

The equilibrium constants for most of the studied reactions were calculated with the theoretically highest possible accuracy, including the changing thermal capacity of the substances reacting with the temperature. The required thermodynamic magnitudes (ΔH_{298}^0 , S_{298}^0 , Cp_{298}^0 , and the thermal capacity equation factors a, b, and c) were taken from the reference book [14]. Whenever the a, b and c coefficients were not known for all the reacting substances, we took into account only the changing thermal capacity produced by the reaction. It should be pointed out that the difference between the equilibrium constants obtained in the calculations in the first and the other cases was insignificant.

There are also other methods of computing ΔZ and K reactions whereby pretabulated magnitudes [5, 19 and 24] are used with a view to simplifying the calculations. All these methods produce approximate results, but with auxiliary tables it is impossible to compute the equilibrium constants at intermediate temperatures for which the tables do not contain any calculated coefficients. The calculation system used in this study is therefore more universal, and not very labor-consuming when the simplest types of calculating machines are used.

If the equilibrium constant of the reaction at a given temperature is known, it is easy to find the composition of the equilibrium gas mixture (fluid) which is expressed by the partial pressure or volatility (fugacity) of the components. In view of the fact that during the metamorphism the total as well as partial pressure of the basic volatile components could amount to hundreds and thousands of atmospheres, when the deviation of the gas properties from the ideal gas is considerable, the expression of the equilibrium constant in partial pressure should be avoided. In this study we have calculated the magnitude K_f , a thermodynamic equilibrium constant, which is not dependent on pressure. A comparison of the equilibrium constant K_f (expressed by the volatility of the components in a mixture of real gases) with the equilibrium constant K_p (expressed by the partial pressure in a mixture of ideal gases) shows that when the pressure is low enough and the mixture of real gases is governed by the law of ideal gases, K_f is equal to K_p . When the pressure is high, there is a considerable difference between K_f and K_p . The computation of this difference, that is the transition from K_f to K_p , is required for the precise calculation of the pressure effect on the stability range of the minerals and the composition of the equilibrium gas mixture. This is a very complicated problem, and it can be solved with a fair degree of accuracy only in the areas of moderate pressure, assuming that the mixture of real gases is ideal and that the Lewis and Randall rule can be applied to it. The theoretical substantiation of such calculations and examples of their practical application can be found in the special studies [4 & 8]. In the case of metamorphic processes, these questions require a separate consideration which is beyond the scope of this article.

The above observations should be taken into consideration when proceeding from the data obtained on the basis of thermodynamic calculations to the actual conditions existing in the period of metamorphism. The equilibrium constants of the reactions and the stability range of the minerals referred to below are expressed in terms of the volatility of the gas components as is usually done in the contemporary studies dealing with the use of thermochemistry for the solution of petrological problems, as

for example in H. Holland's study [34]. The switch to partial pressures in certain diagrams is due to the assumption that, in the first approximation, the gas volatility is equal to its partial pressure.

The method of constructing a diagram of mineral stability as a temperature and volatility function of the components of the equilibrium gas mixture is not very difficult, and does not require any special examination. The methods of constructing such diagrams are described in great detail by P. Harrels [6] for low T and p regions; the only difference in the construction of similar diagrams for high T and p values is that the volatility of the components is substituted for their partial pressure. The limited scope of this article, and particularly the diagrams, prevent a fuller description of the effect of high pressures on the range of mineral stability.

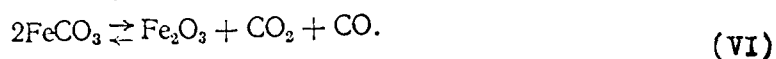
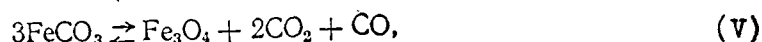
The results of the thermodynamic calculations and
the diagrams of the stability range

The resulting data are graphically presented in the form of curves $\lg K_f = f(T)$ for all the theoretically authentic dissociation and oxidation reactions of FeCO_3 , as well as the reactions produced by the dissociation of the solid and gaseous phases that are present in the systems. The calculated reaction equilibrium constants were used for the construction of diagrams showing the stability range of siderite and ferric oxide. The metastable associations are deleted from these diagrams. Nor are the possible methods of reducing FeCO_3 and the products of its conversion to ferrous metal discussed, inasmuch as these reactions are not very probable in natural conditions. In the calculations and diagrams we used a temperature range of 25-600°C.

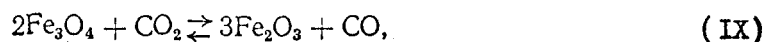
The following possible basic variants are analyzed to show the characteristic features of the metamorphic transformation of siderite in various media: a) the change of siderite in a neutral dry medium (with free oxygen and water absent from the system); b) the change of siderite in the presence of water (with free oxygen absent from the system); c) the change of siderite in the presence of free oxygen.

The $\text{FeO-CO}_2\text{-CO}$ system

The thermal dissociation process of siderite in a neutral medium which contains no free oxygen or water can be described by the following direct reactions:



We must also include the succeeding oxidation-reduction reactions which may theoretically occur in the case of a step-like dissociation of siderite.



The possible variant reactions involving the reduction of CO_2 and CO to C are not cited because their likelihood is very small.

The stable correlations between the ferrous compounds (FeCO_3 , FeO , Fe_3O_4 and Fe_2O_3) in this system can be expressed only in form of function f_{CO_2} as well as f_{FeO} and f_{CO} (it is, of course, understood that stability is also a temperature function). It should be pointed out that the description of siderite stability in geological literature merely as a function P_{Fe_2} [6 and 13] or f_{Fe_2} [34] is obviously inadequate as it does not take into account the possible oxidation of the x bivalent iron compounds by carbonic acid. Some geological publications [3] contain references to the oxidizing effect of CO_2 on the processes of abyssal mineral formation, but such an effect is not evaluated.

As the thermodynamic calculations show, in the oxidation of Fe^{2+} compounds the carbonic acid is reduced to CO , and in the case under consideration FeCO_3 or FeO should be converted to Fe_3O_4 or even Fe_2O_3 . The probability of such a process becomes obvious by an examination of the curve $\lg K_f = f(T)$ of the reaction involving the transformation of siderite into magnetite (Fig. 1, curve V), which at temperatures above 175°C is located higher than the analogical curve IV of the reaction whereby siderite is converted to FeO with only a CO_2 discharge. An increase in temperature shifts the equilibrium in these reactions to the right, and considerably widens the gap between the equilibrium constants (with 500°C K_f of reaction IV equal to $10^{3.7}$, and reaction V to $10^{10.2}$).

The further oxidation of the formed magnetite to hematite by carbonic acid in reaction IX can occur only at a very low f_{CO} value, and the achievement of these in ferrosilicon rocks containing siderite is not very probable. Our data fully coincide with those of J. Hawley and S. Robinson [33] who reached the conclusion that it is impossible to oxidize magnetite by carbonic acid discharged during the assimilation of limestone with granodiorite magma in the process of contact metasomatic layer formation.

The conclusion that the decomposition of siderite results in the formation of magnetite as a stable mineral within a wide range of f_{FeO_2} and f_{CO} values may be drawn also from the curves $\lg K_f = f(T)$ of the IV, VII, VIII and IX reaction (Fig. 1) which describe the same dissociation process of siderite but on the assumption that it is characterized by a stepwise course: the decomposition of siderite into FeO and CO₂ took place first, and the oxidation of FeO with the release of carbon dioxide next. The oxidation of FeO can also end in the formation of Fe₃O₄ (reaction VII) without continuing to the formation of Fe₂O₃ because the last reaction (IX) is characterized by very low K_f magnitudes for all the temperatures under consideration.

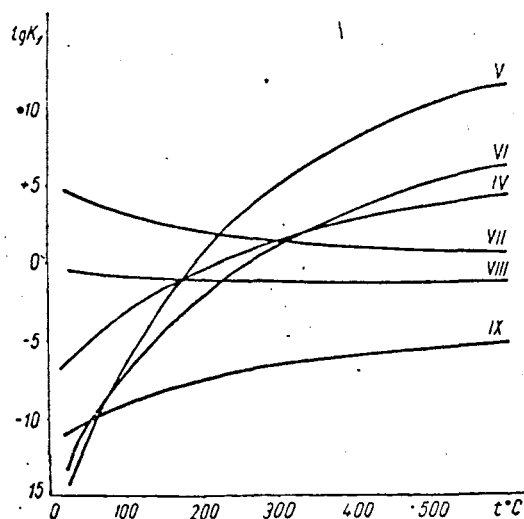
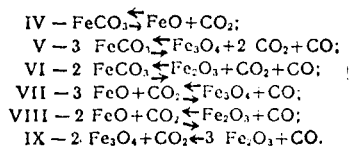
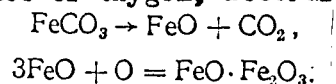


Fig. 1. The relationship between the logarithm of the equilibrium constant and the temperatures required for the reactions:



Some authors [267] believe that siderite is transformed into magnetite during the metamorphism in the presence of oxygen, according to the following scheme:



The above-cited data make it clear that such an assumption is absolutely unnecessary; furthermore, with a constant supply of oxygen siderite should be converted to hematite, rather than magnetite, as will be shown later.

The stability range of siderite and ferric oxides in the coordinates $\lg f_{\text{CO}_2}$, $\lg f_{\text{CO}}$ and $T^\circ\text{C}$ is shown on the diagram (Fig. 2). The isothermal crosscut of the diagram for 400°C is shown in Fig. 3.

The part of the diagram limited by the magnitude $\lg (f_{\text{CO}_2} + f_{\text{CO}})$ not above 4, which in the first approximation corresponds to the total pressure of these components of 10,000 atmospheres, may have some practical value for an analysis of the metamorphic processes. The stability range in the field of higher $\lg (\sum f)$ values has only illustrative significance.

Clearly seen on the diagram (Fig. 2) is that the stability fields of siderite are reduced with increasing temperature and a corresponding expansion of the magnetite, hematite and FeO. The quantitative values of the equilibrium volatility of CO_2 and CO for each mineral or mineral association at any temperature can easily be determined directly from the diagram. It would be more convenient to construct such a diagram by the use of isothermal crosscuts (Fig. 3) and supplement them with isobaric curves. For example, the equilibrium gas mixture found from the graph for a siderite-magnetite association at a temperature of 400°C and a total volatility of 1,100 is characterized by f_{CO_2} -1000 and f_{CO} -100 which, in the first approximation, corresponds to P_{CO_2} -1000 atmospheres and P_{CO} -100 atmospheres, with a ratio of P_{CO_2} - P_{CO} ratio of 10:1. The f_{CO} increase occurs before the conversion of magnetite to siderite, and the f_{CO} reduction before the reverse process. The stable existence of Fe_2O_3 at high temperatures in paragenesis with siderite is possible only at high f_{CO_2} and very low f_{CO} . Above 300°C , the equilibrium existence of this association would require a partial CO_2 pressure above 10,000 atmospheres, which is not very probable under natural conditions. Equally improbable are an association of siderite with FeO and the independent

existence of FeO which are possible only at high f_{CO} and very low f_{CO_2} values.

What is important is that the boundaries between the stability fields of ferric oxides are determined primarily by f_{CO} itself.

The resulting data serve to emphasize the importance of CO in the metamorphic processes which should not be disregarded when analyzing the conditions of the genesis and existence of ferrous minerals and their associations.

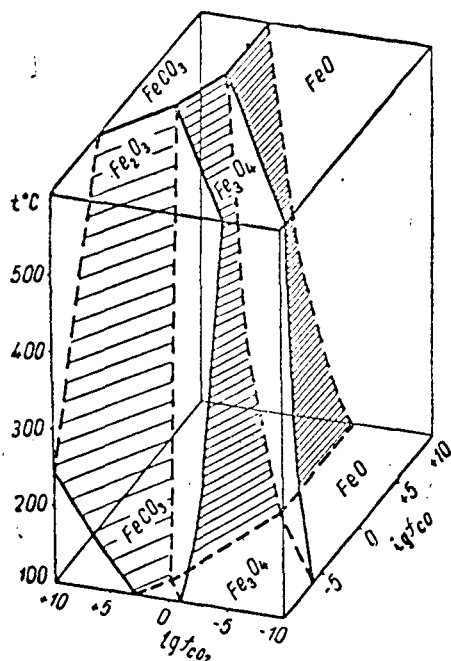


Fig. 2. Diagram of the stability fields of siderite and iron oxides in the coordinates $\lg f_{CO_2}$, $\lg f_{CO}$, and $t^{\circ}C$.

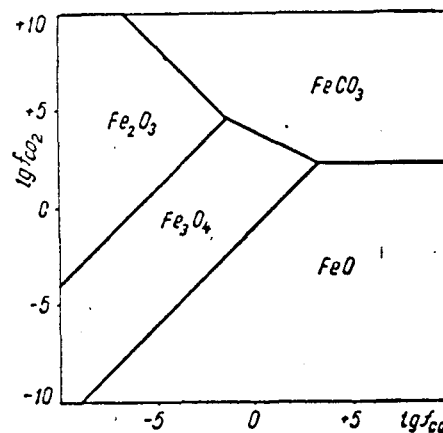


Fig. 3. Isothermic cross section at $400^{\circ}C$ of the $\lg f_{CO_2}$ - $\lg f_{CO}$ - T diagram of the FeO-CO₂-CO system.

We will further define the curves $P_{CO_2} = f(T)$ of the Goldschmidt-Korzhinskiy reactions I, II and III (Fig. 4). The first of these reactions is a partial case of the system under study, and it agrees with the multivariant curve in Fig. 2 or the invariant point in Fig. 3 (with $T = \text{const.}$) for the equilibrium association of siderite-magnetite-hematite. Mention should be made here of the displacement of this curve in the area of lower temperature, as well as the fact that the existence of this mineral association as an equilibrium association is possible only at low P_{CO} values. Two other reactions are indirectly related to the system under study inasmuch as they include SiO_2 and iron sulfides. The curves $P_{CO_2} = f(T)$ of these reactions are also considerably different from those cited in the previous studies.

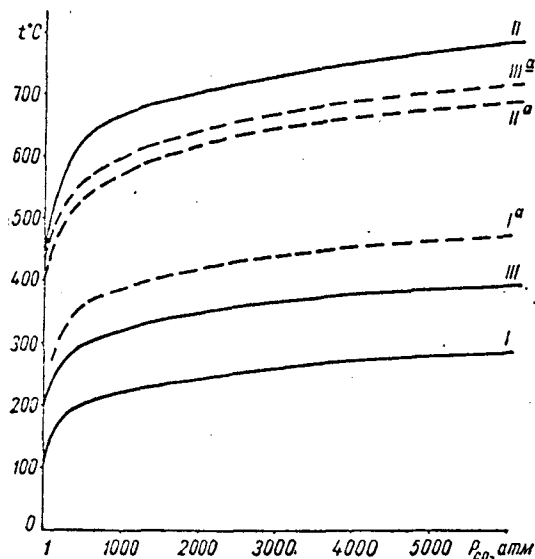
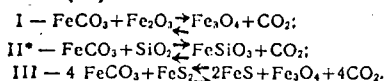


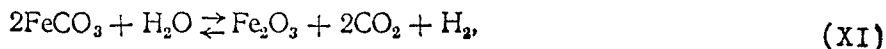
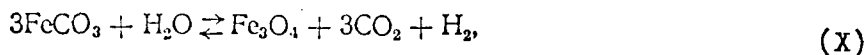
Fig. 4. Curves $P_{CO_2} = f(T)$ of the decarbonization reactions:



The curves $P_{CO_2} = f(T)$ of the same reactions (I^a , II^a , III^a), according to D. S. Korzhinskiy, are presented for purposes of comparison with the dotted lines.

The $FeO - H_2O - CO_2 - H_2$ system.

The possible oxidation reaction of siderite and its dissociation products by water are discussed in this system.



These constructions were made on the assumption that free oxygen was absent from the system, and that the dissociation of the siderite in reactions V and VI did not take place. The latter assumption is fully substantiated from a thermodynamic point of view.

There are references in some geological studies to water as the possible natural oxidizer [3 and 27], but only V. Mann [36] comes to the conclusion, on the basis

* The calculation of reaction II involved the replacement of the quartz value ΔH_{298}^0 , cited in the table, by a new value -217.7 kilocal./mole.

of thermodynamic calculations, that the oxidation of magnetite into hematite by water is not very probable. We have shown [16] that at high temperatures water can oxidize siderite into magnetite. A further oxidation into hematite is not practical.

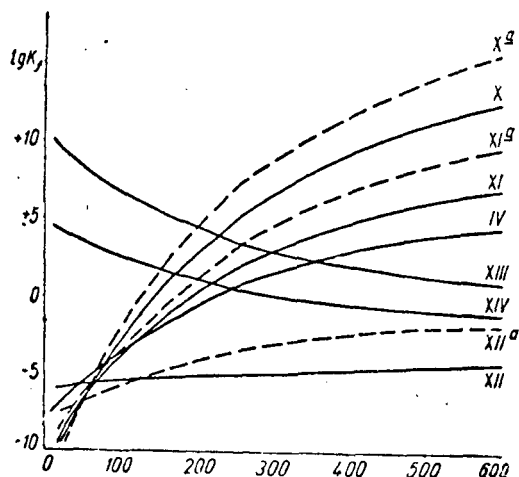
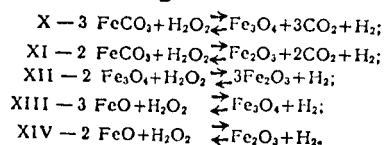


Fig. 5. The dependence of the logarithm of the equilibrium constant on temperature in regard to reactions:



The dotted lines are presented for analogical reactions (X^a , XI^a and XII^a); the curves $\lg K_p = f(T)$ are calculated on the assumption that the water present in the reaction was not in a gaseous (H_2O_g) but a liquid (H_2O_l) phase.

Calculations show that siderite is stable at relatively low temperatures in the presence of gaseous or liquid water (the solubility of siderite at low temperatures in solutions with different pH and Eh values, as well as the reduction-oxidation reactions in the hypergenetic zone, are not discussed here as they have been studied in detail by R. Barreils [6]). At 25°C, the equilibrium constants of all possible siderite oxidation reactions by water have very low values (Fig. 5), but as the temperature rises the equilibrium in reactions X and XI reveals a sharp turn toward the development of magnetite and hematite. At 130-140°C, the oxidation of siderite into magnetite K_f by water equals 1, and at 500°C it amounts to 10^{11} for reaction X and $10^{13,18}$ for reaction X^a . Let us look at a case characterized by a step-like process: The breakdown of FeCO_3 into FeO (reaction IV) followed by the oxidation of

FeO in reactions XIII and XIV (Fig.5) with water, support the conclusion on the oxidizing effect of water. The cited curves show that the FeO produced by the thermal dissociation of siderite will be oxidized into magnetite; the oxidation Fe_2O_3 (reaction XII) in geological conditions is practically impossible inasmuch as it requires a very high $f_{\text{H}_2\text{O}}$ value and an insignificant f_{H_2} . A better graphic description of the relationship between the iron compositions in this system is provided by the diagram (Fig. 6) constructed for 400°C.

It is characteristic that at temperatures above 100°C, the magnitudes K_f of the oxidation of FeCO_3 and Fe_3O_4 by liquid water (X^a , Xl^a and Xll^a) exceed the K_f magnitudes of similar reactions involving gaseous water (X, Xl , and Xll), even though the nature of the curves in Fig. 5 is the same. A change from K_f to K_p and the introduction of an appropriate correction for pressure will reveal that in the case of T and p, which are supercritical for water, the actual curve $\lg K_p = f(T)$ will occupy some intermediate position. Hence the important conclusion that the aggregation of water in the above-reviewed metamorphic processes had little effect on the direction of the irreversible reactions involving water at high temperatures.

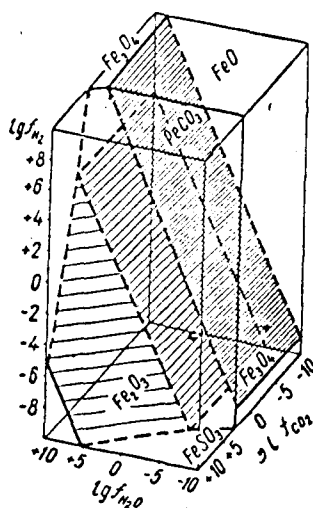


Fig. 6 Isothermal diagram of siderite and ferric oxide stability at 400°C in coordinates $\lg f_{\text{H}_2\text{O}}$, $\lg f_{\text{CO}_2}$ and $\lg f_{\text{H}_2}$.

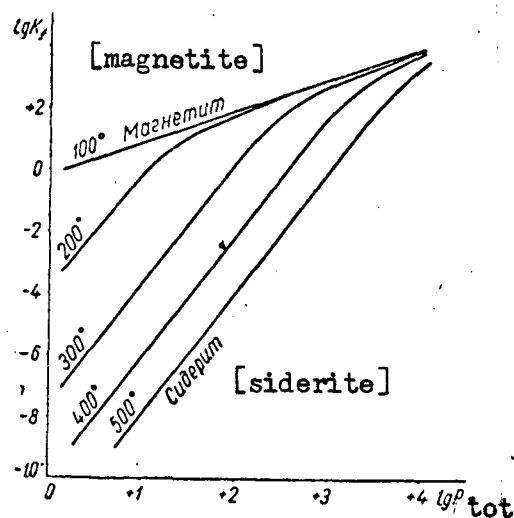


Fig. 7. Diagram of siderite and magnetite stability range, depending on total pressure ($\lg P_{\text{tot}}$) partial pressure ($\lg P_{\text{H}_2\text{O}}$) and temperature.

A comparison of curves $\lg Kf = f(T)$ of the sideration dissociation reaction in a dry neutral medium V, and the oxidation reaction of FeCO_3 by water into $\text{Fe}_3\text{O}_4\text{-X}$, will show that the curve of the first reaction is lower than that of the second. Similarly arranged are the curves representing the oxidation of FeO by carbon dioxide (VII) and water vapor (XIII). Thus if the metamorphosed iron ore contained water, the rising temperatures made the siderite unstable and changed it to magnetite, not because of the usual thermal dissociation including the release of CO_2 and CO , but as a result of the FeCO_3 oxidation by water and the release of CO_2 and molecular hydrogen. An increase in pressure, according to the Le Chatelier principle, will shift the equilibrium in the direction of siderite stability but, as the calculations show, even under a pressure of several thousand atmospheres FeCO_3 reacts with water and produces Fe_3O_4 at a temperature range of 400-600°C. A more graphic description of the effect of pressure on the stability range of siderite and magnetite can be seen in the diagram (Fig.7) where such ranges are shown at low temperatures in the $\lg P_{\text{tot}}$.

($P_{\text{tot.}} = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} + P_{\text{H}_2}$) and $\lg P_{\text{H}_2\text{O}}$ coordinates. On that diagram it is easy to find the fraction of the water vapor in the equilibrium gas mixture for any T and p, as well as the composition of that mixture. For example, at 400°C and a total pressure of 1000 atmospheres, the composition of the equilibrium mixture, expressed in partial pressures, is: $P_{\text{H}_2\text{O}} = 65$ atmospheres, $P_{\text{CO}_2} = 700$ atmospheres and $P_{\text{H}_2} = 235$ atmospheres. These figures are very approximate as they have been calculated on the assumption that the mixture is governed by the laws of ideal gases; but they provide a general idea of the important role of water as an oxidizer, and the role of hydrogen in metamorphic fluids. As the temperature rises, the concentration of hydrogen in such fluids should greatly exceed the concentration of water vapor or liquid water.

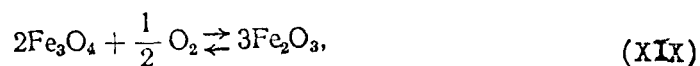
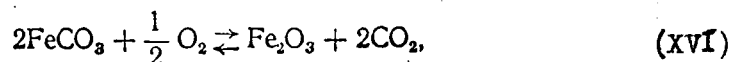
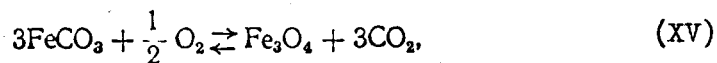
The above-cited diagram (Fig.7) clearly shows the reciprocal effect of temperature and pressure on siderite and magnetite. A rise in temperature increases the stability range of Fe_3O_4 , and an increase in pressure reduces that range by a corresponding expansion of the FeCO_3 stability range.

Thus whenever the metamorphism of ferruginous sedimentations took place in the

presence of water, one of the major volatile components must have been hydrogen whose concentration (or volatility or partial pressure) largely determined the conditions of the development and stability range of the iron minerals.

The FeO-CO₂-O₂ system

The following possible oxidation reactions of siderite and its dissociation products with free oxygen;



are characterized by very high Kf values (Fig.8) which indicates that siderite becomes unstable and changes to magnetite or hematite even at absolutely low f_{O_2} values. Thus at 500°C, FeCO₃ begins to change into Fe₃O₄ as it reaches and maintains the f_{O_2} during the reaction, which corresponds to a partial oxygen pressure of only 10⁻²⁹ atmospheres (with P_{CO₂} less than 3000 atm.); Fe₃O₄ remains stable within the range of P_O 10⁻²⁹-10⁻¹⁸ atm., and changes to Fe₂O₃ at higher P_O values (also at corresponding P_{CO₂} values). A reverse change of hematite to magnetite at this temperature is possible only at P_{O₂} values and lower than 10⁻¹⁸ atmospheres. Shown in the diagram (Fig.()) is the stability range of the iron compounds in the coordinates lgf_{O₂}, lgf_{CO₂}, and T; the equivalent values of f_{O_2} and f_{CO_2} for each mineral association in connection with the temperature can be found directly from the diagram.

A study of the natural mineral associations of metamorphic rocks failed to reveal any proof of the role of free molecular oxygen (and a corresponding increase in f_{O_2}) in the metamorphism. Generally, the metamorphic processes took place at very low f_{O_2} values. This conclusion is supported also by the theoretical and experimental investigations carried out by G. Eigster [29 and 30] whose data on the Fe-O system are

close to ours.

On the whole, the diagram cited in Fig. 9 serves as a generalized scheme, inasmuch as the above-discussed diagrams (Figs. 2 and 6) represent particular cases of this diagram. This deduction is explained by the fact that the oxidizing capacity of H_2O and CO_2 is conditioned by the thermal dissociation reactions:



The equilibrium constants of these reactions (Fig. 10) have low values, but at temperatures of 150-200°C the equilibrium f_{O_2} , calculated for reactions XX and XXI, is already close to the f_{O_2} equilibrium of reaction XV and even XVII, and above 200°C it exceeds them to such an extent whereby $FeCO_3$ or FeO can be oxidized into magnetite. It is interesting that at equal temperatures the Kf magnitudes of reaction XX are always greater than reaction XXI, that is the water in the conditions of metamorphism has a greater oxidizing capacity than CO_2 which is fully confirmed by the data of the preceding sections.

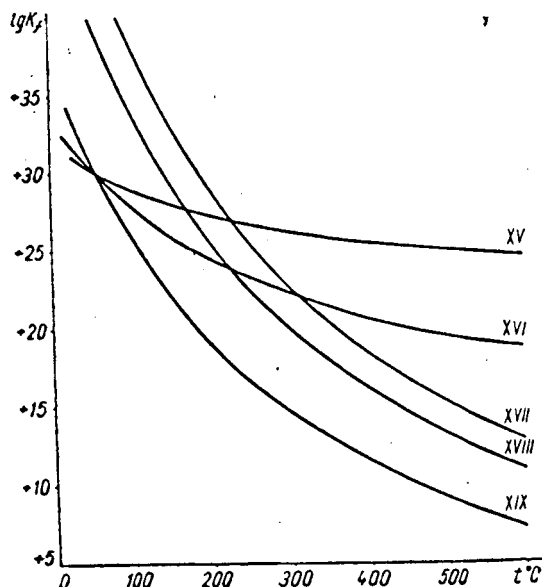


Fig. 8. The relation between the equilibrium constant logarithm and the temperature in the following reactions:

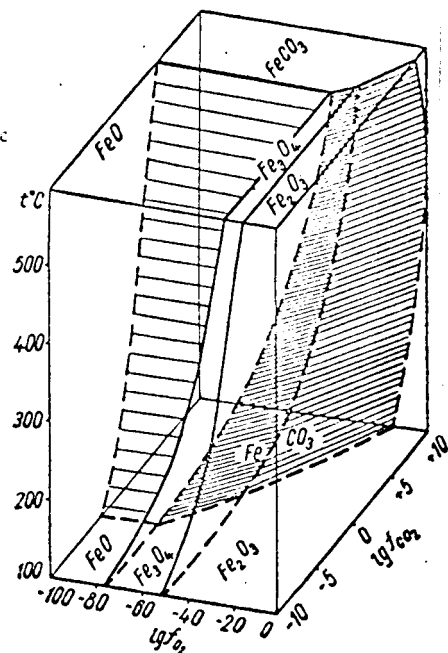
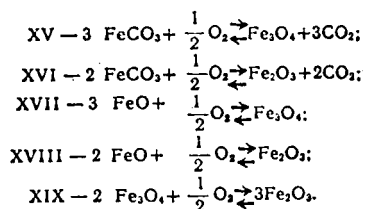


Fig. 9. Diagram of siderite and ferrous oxide stability ranges in coordinates $lg f_{O_2}$, $lg f_{CO_2}$, and $t^\circ C$.

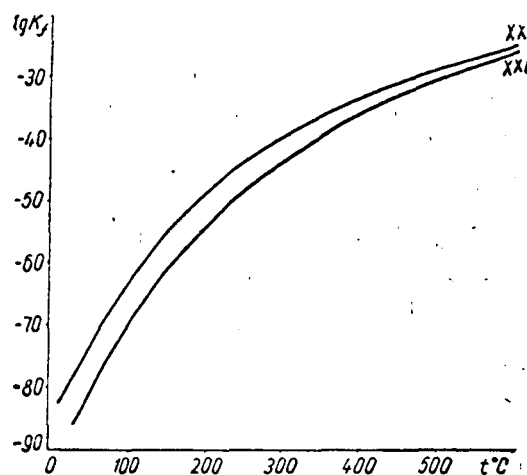
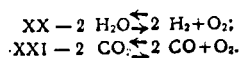


Fig. 10. The relation between the equilibrium constant logarithm and the temperature in thermal dissociation reactions of water and CO_2 :



It appears from curve $\lg K_f = f(T)$ of reaction XIX and the diagram (Fig. 9) that at temperatures up to 600°C hematite can change to magnetite only at very low f_{O_2} values which could not have emerged during the metamorphism of homogeneous hematite (goethite) rocks, if the others did not contain any reducing agents (organic rock, siderite, etc.). The presence of H_2O or CO_2 in the metamorphic rocks will always maintain a fairly high f_{O_2} value in order to prevent a direct change from hematite to magnetite rocks. The predominance of magnetite in ferruginous rocks in the lower and middle stages of the metamorphism indicates that it had developed either from siderite or mixed siderite-hematite rocks; in the latter case the f_{O_2} value was low enough to facilitate the conversion of hematite to magnetite.

General Geological Conclusions

M. P. Semenenko [22] classifies the ferruginous quartzites and schists containing siderite as metamorphic schist which developed at temperatures up to $375\text{--}400^\circ$. Considerably higher temperatures are mentioned in V. S. Sobolev's studies [23]; thus the boundary of the low- and medium- temperature metamorphism is estimated at 600°C , and the temperature of the lower boundary of the regional metamorphism at $450\text{--}500^\circ\text{C}$.

According to F. Turner and J. Ferhugen [25], the temperature at the time of the formation of the metamorphic facies of greenstone slate fluctuated between 300 and 500°C. The pressure, according to various authors, may have fluctuated from 1000 to 8000 atm.

It appears from the adduced theoretical data that siderite becomes unstable at temperature believed to exist at the lower boundary of the regional metamorphism, and should change to magnetite. In the presence of gaseous or liquid water this conversion takes place at still lower temperatures. Above 400°C, siderite is capable of a stable existence only under great pressure (over 5,000 atm.), or an insignificant f_{H_2O} which may occur in the limited content of interstitial water. The equilibrium siderite-magnetite association is a buffered association, that is it can exist at a given temperature and total pressure only with definite and precisely defined magnitudes of f_{H_2O} and other volatile components in an equilibrium mixture.

The relative quantities of individual solid phases do not affect the composition of such a mixture, but a change in the concentration of even one of the volatile components will produce a change in the relative quantities of the solid phases (as a result of heterogenic reactions) until the original equilibrium composition of the gas mixture is restored. We showed that in the conditions of regional metamorphism, the siderite-magnetite association, which is a buffered association, could exist in a state of equilibrium with a gas mixture with comparatively low f_{H_2O} and high f_{CO_2} , f_{H_2} and a partial f_{O_2} . In the case of an open system, the inflow of new water to the rocks in the process of metamorphism would have led to an increase in f_{H_2O} and a change in the relative mass of magnetite and siderite. In the case of permanent surplus of water in the metamorphic fluids, as some researchers seem to believe, siderite could not remain stable even at comparatively low temperatures (up to 300°C), and could not be retained in the ferruginous quartzites of the Krivoy Rog type. The simplest calculations show that the complete oxidation of siderite to magnetite requires a relatively small quantity of water.

Thus the hypothesis that the magnetite of ferruginous quartzites is formed from primary sedimentary and diagenetic siderite is fully substantiated from a physico-chemical point of view.

The metamorphism of ferruginous rocks which contain siderite in association with magnetite or silicates took place at relatively low temperature, and the lower temperature boundary of the dynamothermal metamorphism (the stage of slate of the green slate facies) must have been 300°C. At higher temperatures the siderite could remain stable only with low f_{H_2O} values, that is with a limited content and inflow of water in the rocks undergoing metamorphism. These data indicate the important role of water in the metamorphic processes of the ferruginous-siliceous rocks. The buffered siderite-magnetite association could maintain a stable existence during the process of metamorphism only with certain equilibrium values f_{H_2O} , f_{CO_2} , f_{CO} , f_{H_2} which could be found as a quantitative expression from the cited diagrams. The change in the volatility of these components in the metamorphic fluids produces as much of an effect on the stability range of the iron-ore minerals as temperature and pressure. Consequently, the number of variables determining the boundaries of the metamorphic facies should include, in the above-discussed cases, not only the temperature and general pressure but also the concentration (volatility and partial pressure) of the volatile components H_2O , CO_2 , H_2 and CO .

A comparison of the paragenetic association of ferruginous rocks containing siderite with the temperature conditions of their formation justifies the conclusion that in many cases, as in the paragenesis of siderite with cummingtonite for example, the progressive metamorphic process took place in conditions of limited partial water pressure. Hence the logical conclusion that the siderite-chlorite, siderite-magnetite and siderite-cummingtonite associations, for example, were formed at similar rather than different temperatures but under different partial water pressures. The latest information supports the criticism of the concept that water was present everywhere as a free phase during the metamorphism [10 and 18].

The available theoretical data justify the assumption that considerable quantities of molecular hydrogen were released during the metamorphism of siderite-containing ferruginous rocks. Preliminary calculations show that during the metamorphic process of such rocks with an iron content usual for Krivoy Rog, even if we assume that only half of the iron was originally included in the siderite, one cubic meter of rock could

release up to 50 m^3 of hydrogen (calculated in terms of normal conditions), or $5 \cdot 10^{10} \text{ m}^3 \text{ H}_2$ from one cubic meter. The formation of H_2 in the siderite-oxidation and other natural iron oxides reactions with water accounts in some measure for the emergence of depth hydrogen.

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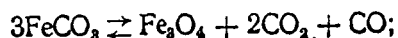
Article submitted on
28 March 1964

THEORETICAL DATA ON THE STABILITY OF SIDERITE IN THE PROCESS OF METAMORPHISM

Resumé.

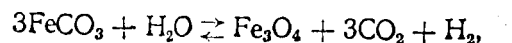
Thermodynamic calculations are used in this article to determine the boundaries of the stability range of siderite and iron oxides, depending on the temperature, general pressure and concentrations (expressed in terms of volatility) of the basic components of metamorphic fluids-- H_2O , CO_2 , H_2 , CO and O_2 . All the possible siderite dissociation reactions and the following reduction-oxidation reactions in various media have been discussed: a) in a neutral dry medium (free oxygen and water are absent); b) in a water medium (free oxygen absent); c) in an oxygen-containing medium.

Siderite dissociation in a dry neutral medium should take place in the following generalized reaction:



the further oxidation of magnetite to hematite by carbon dioxide during the metamorphic period is not very probable, as Fe_3O_4 represents a stable solid phase within a wide range of f_{CO_2} and f_{CO} values.

The following generalized reaction is of major importance in the presence of water as a free phase in the metamorphic rocks:



the equilibrium constants of this reaction above 150-200°C exceed 1 and are higher than the equilibrium constants of the siderite dissociation reaction in a waterless medium.

Thus in the low and middle stages of dynamothermal metamorphism, siderite is unstable and should change to magnetite even in the absence of oxygen. The presence of water reduces the temperature of this changing process, and the increase in pressure raises it. The above-cited diagrams of the stability range in the $\text{FeO}-\text{CO}_2-\text{CO}$ and $\text{FeO}-\text{CO}_2-\text{H}_2\text{O}-\text{H}_2$ systems make it possible to calculate the composition of the equilibrium gas mixture (fluid) for any mineral or mineral association at the temperatures and under the pressures existing in the metamorphic period. It has been established that at temperatures of 400-600°C and under pressures of several thousand atmospheres siderite can maintain a stable existence only in a state of equilibrium with a fluid characterized by low $f_{\text{H}_2\text{O}}$ values and very high f_{CO_2} and f_{H_2} values.

The discovery of siderite in association with magnetite or ferruginous silicates in the metamorphosed ferruginous quartzites is indicative of the relatively low temperature of the metamorphism of these rocks. At any rate, the lower temperature boundary of the dynamothermal metamorphism (the slate stage of the greenstone slate facies) did not exceed 300°C. The siderite could have remained stable at higher temperatures only in case of a limited content and inflow of water into the metamorphosed rocks. A comparison of the paragenetic associations of the siderite-containing ferruginous rocks with the assumed conditions of their formation justifies the conclusion that in many cases the progressive metamorphism took place under very limited partial water pressure. The assumption appears to be well-grounded that the siderite-chlorite, siderite-magnetite and siderite-cummingtonite associations, for example, were formed at the same, rather than different, temperatures, but under different partial water pressure. The number of variables determining the boundaries of the metamorphic

facies in the above discussed cases should therefore include not only the temperature and general pressure but also the concentrations (volatility and partial pressure) of the volatile components H_2O , CO_2 , H_2 , and CO . The assumption is made, in conclusion, that molecular hydrogen is released by the siderite-containing ferruginous rocks in the process of metamorphism.